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solvents. It is a more rapid hydrogenation catalyst than the chloride.[6]

Although the *iodide* can be prepared,[6] it is difficult to obtain in a pure state, free from admixed dimeric product $[(C_6H_5)_3P]_2RhI_2Rh[P(C_6H_5)_3]_2$.

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## 13. IODO(TRIMETHYL)PLATINUM(IV)

$$3CH_3MgI + K_2PtCl_6 \rightarrow PtI(CH_3)_3 + MgI_2 + 2MgCl_2 + 2KCl$$

**Submitted by D. E. CLEGG* and J. R. HALL***
**Checked by C. H. BRUBAKER, JR.,† G. L. GILBERT,† and M. DYKE†**

The preparation of iodo(trimethyl)platinum(IV) of empirical formula $PtI(CH_3)_3$ was first reported by Pope and Peachey.[1] The substance was produced by the reaction between platinum(IV) chloride and methylmagnesium iodide. Gilman et al.[2] have repeated this method of preparation to give a 45% yield and have identified some of the side products of the reaction. Various starting materials and procedures have been used by

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other workers,[3,4,5] and yields up to 55% have been obtained. However, these methods suffer from the disadvantages of inconvenient starting materials, the number of intermediate steps, time involved, and relatively low yields. The procedure described below, carried out under anhydrous conditions, produces $PtI(CH_3)_3$ in 70 to 80% yield in a single step from the readily prepared potassium hexachloroplatinate(IV). Ivanova and Gel'man[4] have previously described the use of potassium hexachloroplatinate(IV) as a starting material. The present modification with excess Grignard reagent and methyl iodide gives superior yields.

### *Procedure*

Solvents and reagents are dried in the following fashion: Benzene and ether are freshly distilled from sodium; methyl iodide is distilled over calcium chloride; and potassium hexachloroplatinate(IV) is dried at 110°.

In a three-necked 500-ml. flask fitted with a reflux condenser, stirrer, and dropping funnel are placed 10 g. (0.02 mol) potassium hexachloroplatinate(IV), 100 ml. benzene, and 50 ml. ether. The reflux condenser is capped with a calcium chloride drying tube. The Grignard reagent is prepared from 3.5 g. (0.14 mol) magnesium, 14.5 ml. (0.23 mol) methyl iodide, and 100 ml. ether by maintaining reflux conditions for 20 minutes. This reaction mixture is filtered through a sintered-glass disk, and the filtrate is placed in the dropping funnel of the three-necked reaction flask.

The reaction flask is cooled in an ice bath and the contents stirred while the Grignard reagent is added over a period of 10 minutes. The ice bath is removed and stirring is continued for 4 hours. The reaction mixture is allowed to stand for about 12 to 16 hours, during which time an off-white solid settles, leaving a clear orange-colored solution.

The reaction flask is placed in an ice bath and while the mixture is stirred, a slurry of 25 g. of ice and 100 ml. of ice-cold

10% hydrochloric acid is very slowly added. The aqueous layer becomes wine-red and the organic layer a deeper orange. The organic layer is decanted and the aqueous layer then extracted three times with 100-ml. aliquots of benzene. Each extraction is carried out under reflux conditions for a period of 20 minutes.

The original benzene–ether layer and the benzene extracts are dried with anhydrous sodium sulfate. After filtration, the organic solution is evaporated to dryness in a stream of air to leave a residue of orange-brown crystals contaminated with some dark-colored material. The latter is removed by washing once with 5 ml. of ethanol. The reaction product is then dissolved in a minimum of chloroform (about 120 ml.). The solution is filtered, the filtrate is evaporated to half its volume, and an equal volume of acetone is then added to give a yellow precipitate. This precipitate is collected, redissolved in chloroform, and precipitated again with acetone. The yie'd is 5.3 to 6.0 g. (70 to 80%). *Anal.* Calcd. for $C_3H_9PtI$: Pt, 53.1; C, 9.78; H, 2.47; I, 34.6. Found: Pt, 52.6; C, 9.95; H, 2.45; I, 34.5. A coarse crystalline orange product may be obtained by recrystallizing the material from hot chloroform.

## *Properties*

Iodo(trimethyl)platinum(IV) is a yellow crystalline product which decomposes at 190 to 195°. It is soluble in most nonpolar solvents and essentially insoluble in polar media such as water and acetone. In benzene solution, the iodo derivative is tetrameric.[6] X-ray investigations have shown that in chloro(trimethyl)platinum four platinum atoms describe a tetrahedron as do the four chlorine atoms, and the two tetrahedra are interpenetrating so as to give a cubic array of platinum and chlorine atoms. Each platinum atom is bonded to three chlorine atoms and to three terminal methyl groups. Some of the trimethylplatinum derivatives of organic chelate ligands are dimeric and in these structures the platinum is again six-coordinate.[7]

Chemically, the platinum-carbon bond in iodo(trimethyl)platinum(IV) is relatively nonreactive and is unaffected by water or oxygen. The iodine atoms may be replaced by other ions through simple metathetical reactions.

A white crystalline material of the composition $PtI(CH_3)_3$ has been obtained in the following fashion.[4] The yellow iodo derivative is converted to the sulfate by metathesis with silver sulfate. Addition of potassium iodide solution to an aqueous solution of trimethylplatinum(IV) sulfate yields a precipitate which, if recovered immediately by filtration, is white, analyzes precisely for $PtI(CH_3)_3$, is free of solvent, and decomposes at 190 to 200°.

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## 14. BIS(2,4-PENTANEDIONATO)ZINC

### (*Zinc Acetylacetonate*)

$$ZnSO_4 \cdot 7H_2O + 2C_5H_8O_2 + 2NaOH \rightarrow Zn(C_5H_7O_2)_2 \cdot H_2O + Na_2SO_4 + 8H_2O$$

$$Zn(C_5H_7O_2)_2 \cdot H_2O + CH_3OH \rightarrow Zn(C_5H_7O_2)_2 \cdot CH_3OH + H_2O$$

$$Zn(C_5H_7O_2)_2 \cdot CH_3OH \rightarrow Zn(C_5H_7O_2)_2 + CH_3OH$$

**Submitted by GUNTER RUDOLPH* and MALCOLM C. HENRY***
**Checked by EARL L. MUETTERTIES†**

Bis(2,4-pentanedionato)zinc, obtained by the action of 2,4-pentanedione on zinc compounds, was long believed to be

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